Hydrodynamically constrained flux of in-situ generated methane hydrate dissolving into undersaturated seawater

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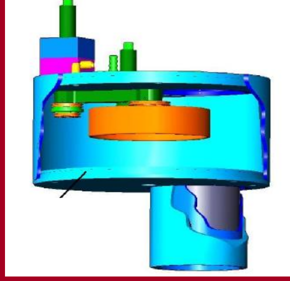
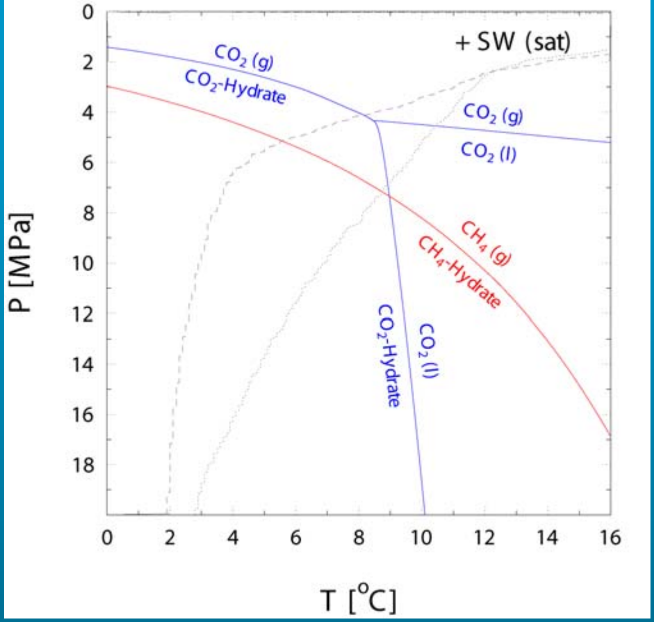
COMET

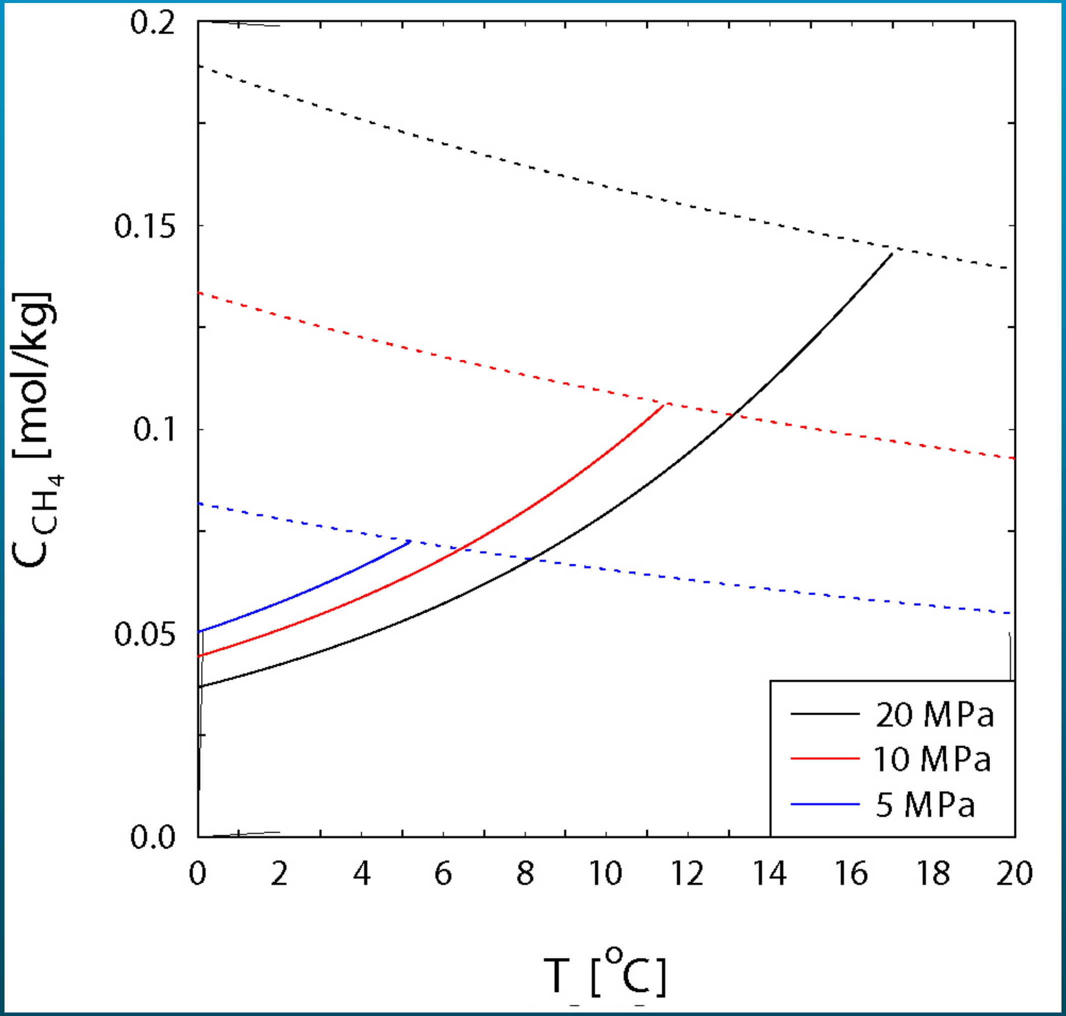
GEOTECHNOLOGIEN

TUHH Technische Universität Hamburg-Harburg

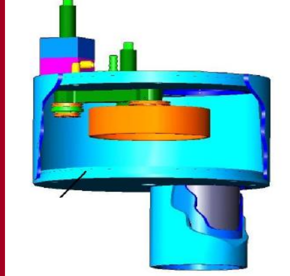
Hydrate stability in seawater

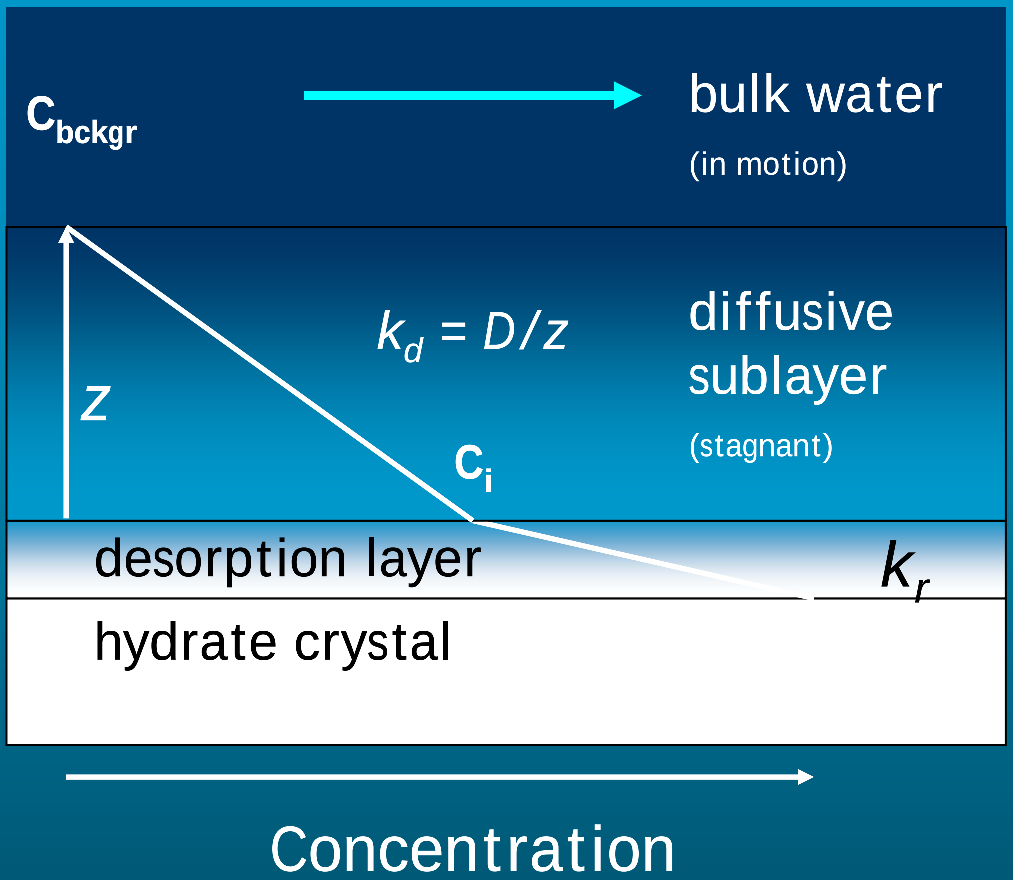






Dissolution of hydrate – diffusion or reaction controlled ?





$F = K´A(C_{sat}-C_{bckgr})$

$$\frac{1}{K'} = \cancel{\frac{1}{k_d}} + \cancel{\frac{1}{k_r}}$$

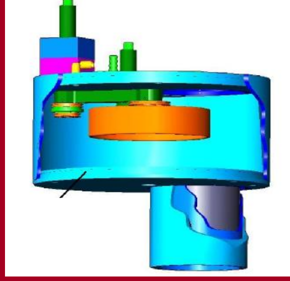
reaction controlled:

$K' = k_r$

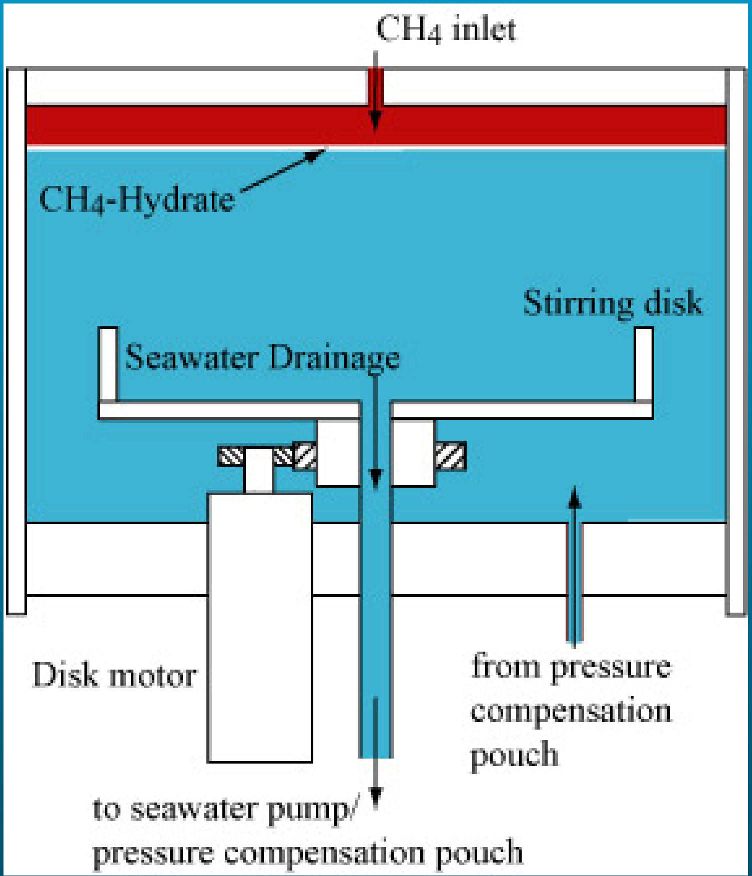
diffusion controlled:

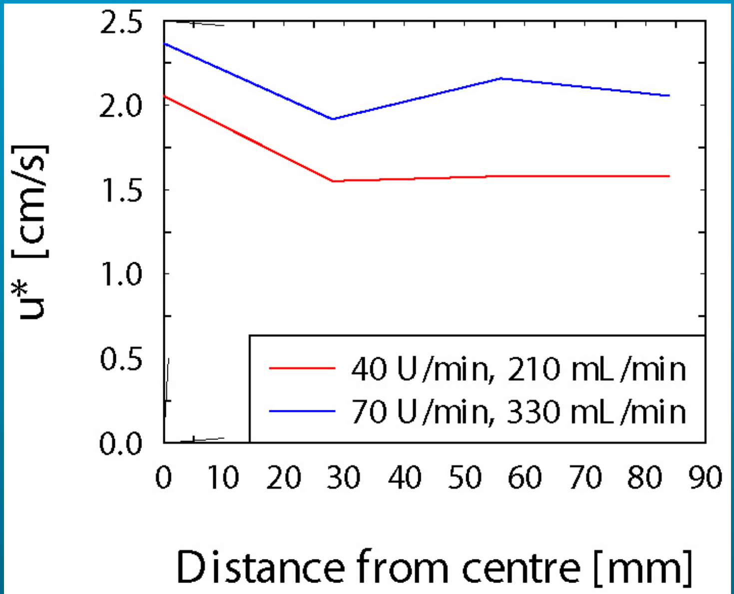
$K' = k_d$

Hydrate dissolution - Tools



Interfacial flux chamber „microcosm“

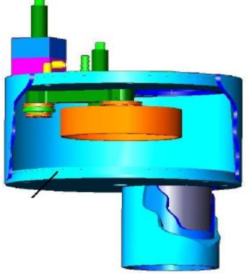


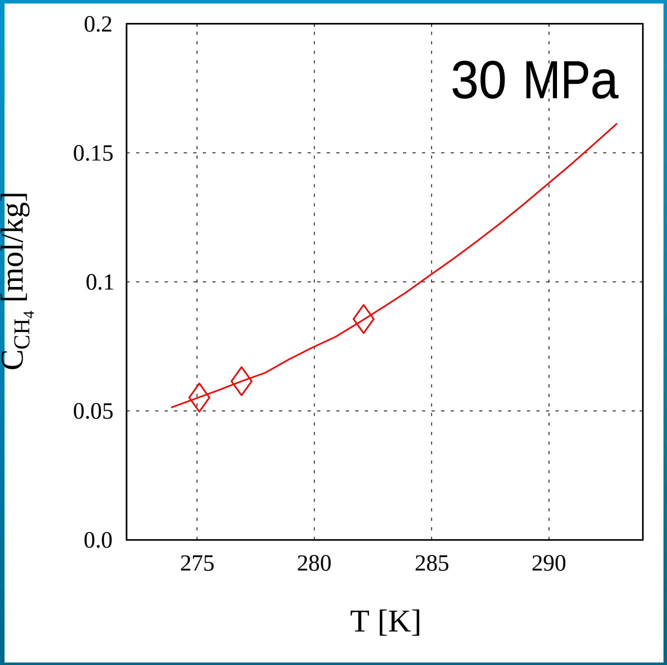


Peppe et al. (1999)

- Production of a radial flowfield at the hydrate/seawater interface in the flux chamber
- Almost constant, adjustable and calibrated friction velocity (*u**) over the entire surface

Hydrate dissolution – Exptl. Parameters



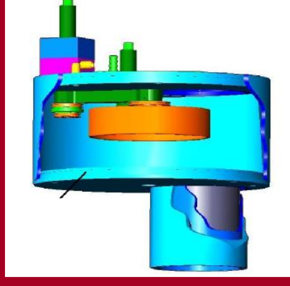


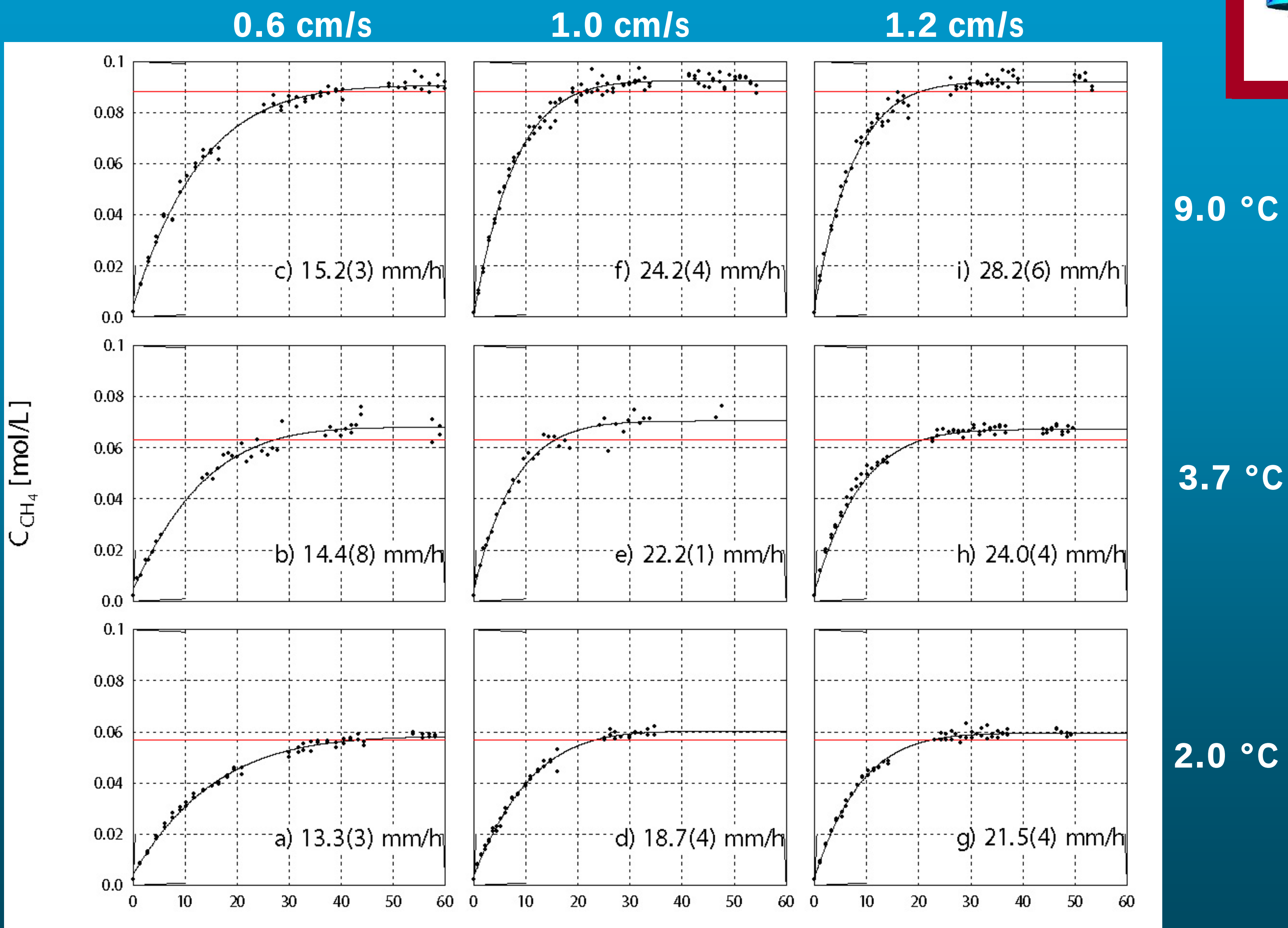
T [°C]	ρ [kg/m^3]	μ [mPas]	$D/10^{-5}$ [cm^2/s]	C_{sat} [mmol/kg]
2.0	1042	1.726	9.306	55.3 (209.9)
3.7	1041	1.638	9.859	61.4 (204.4)
9.0	1040	1.408	11.53	85.8 (189.4)

C_{sat}: Tishchenko et al. (2005)

Friction velocities were set to 0.6, 1.0 and 1.2 cm/s for each temperature

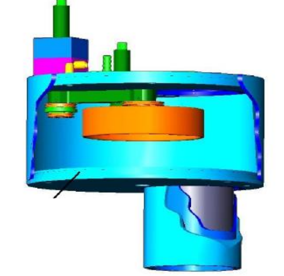
Hydrate dissolution – Results I





$$C_t = C_{t0} + (C_{sat} - C_{t0})\, e^{-(A/V)kt}$$

Hydrate dissolution - Results II

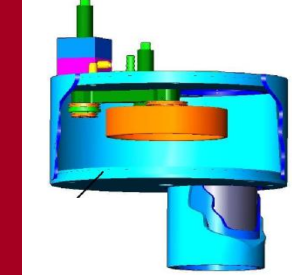


- Saturation concentration in good agreement with predictions according to Tishchenko et al. (2005)
- Change in T results in change of saturation concentration and thus, thermodynamic driving force of dissolution
- Friction velocity (*u**) has a strong impact on the dissolution rate

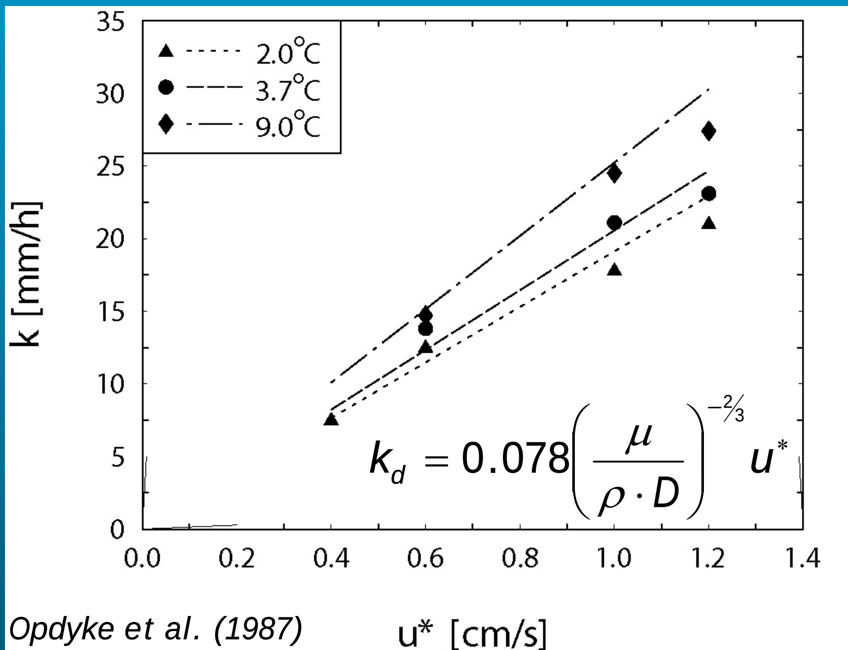
$$\frac{1}{K'} = \frac{1}{k_d} \qquad \frac{dn}{dt} = k_d A\left(C_{sat} - C_{bckgr}\right)$$

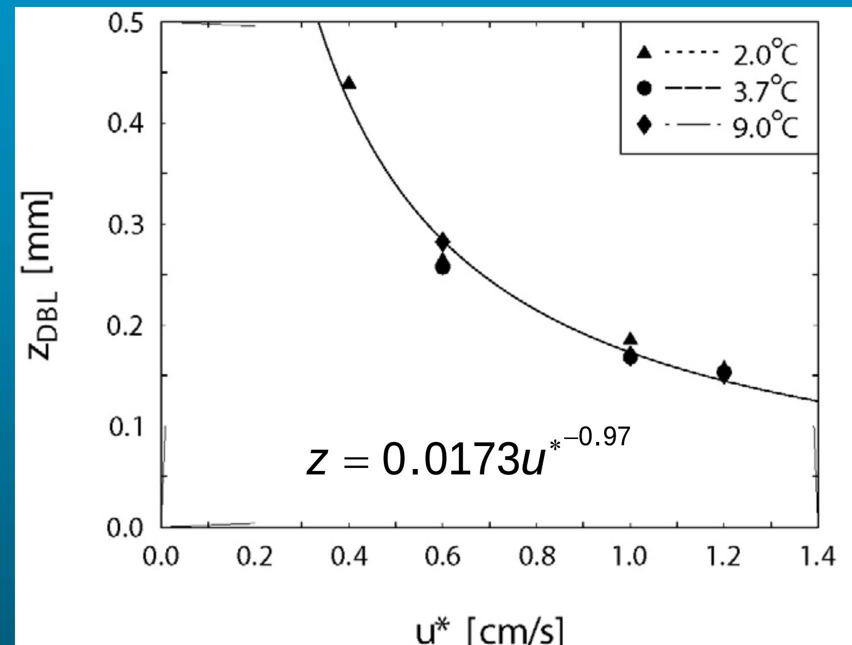
- Results strongly substantiate idea dissolution of methane hydrate in undersaturated seawater is a diffusion-controlled process

Hydrate dissolution - Results III



$$k_d = D / z$$

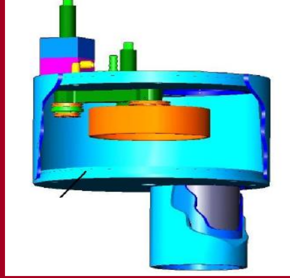




- Excellent agreement of measured transfer coefficients and those obtained from the dissolution of smooth alabaster plates demonstrates reliability of our data.

- Data yield a correlation for the flux of methane from decomposing hydrate outcrops for a broad range of P, T and u* conditions prevailing in the oceans on the seafloor.

Comparison with earlier data



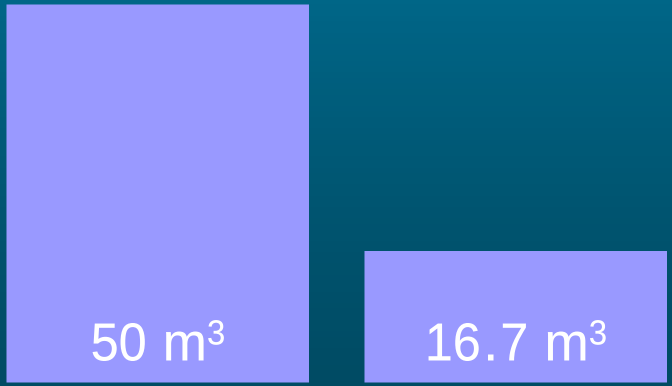
current speed: 1.6 cm/s ->

$u^* = 0.07$ cm/s

$D = 10^{-5}$ cm^2/s

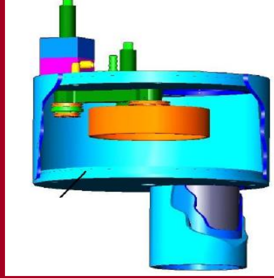
T = 0°C
P = 12 MPa
C_{sat} = 53.7 mmol/L
z = 2.3 mm

T, P, C_{sat} = ?
z = 1 mm



Egorov et al. (1999) | this study

Comparison with earlier data



Egorov et al. (1999)

current speed: 1.6 cm/s ->

$u^* = 0.07$ cm/s

$D = 10^{-5}$ cm^2/s

T, P, C_{sat} = ?

z = 1 mm

50 m^3

this study

T = 0°C

P = 12 MPa

C_{sat} = 53.7 mmol/L

z = 2.3 mm

16.7 m^3

Rehder et al. (2004)

current speed: ? ->

u^* = ?

T = 3.5°C

P = 10.5 MPa

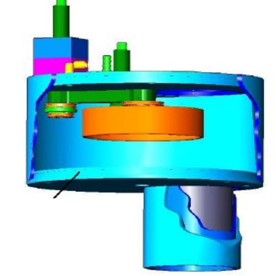
C_{sat} = 69.8 mmol/L

$D = 10^{-5}$ cm^2/s

z = ?

370 µmol

Comparison with earlier data



current speed: 1.6 cm/s ->

$u^* = 0.07$ cm/s

$D = 10^{-5}$ cm^2/s

T, P, C_{sat} = ?

z = 1 mm

50 m^3

Egorov et al. (1999)

T = 0°C

P = 12 MPa

C_{sat} = 53.7 mmol/L

z = 2.3 mm

16.7 m^3

this study

current speed: 1.75 cm/s ->

Hester et al., pers. comm.

$u^* = 0.08$ cm/s

T = 3.5°C

P = 10.5 MPa

C_{sat} = 69.8 mmol/L

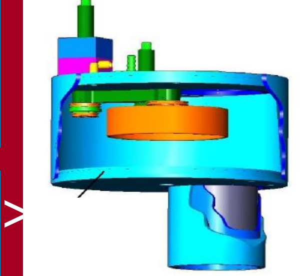
$D = 10^{-5}$ cm^2/s

z = 0.179 mm

370 µmol

Rehder et al. (2004)

Comparison with earlier data



current speed: 1.6 cm/s ->

$u^* = 0.07$ cm/s

$D = 10^{-5}$ cm^2/s

current speed: 1.75 cm/s ->

$u^* = 0.08$ cm/s

Hester et al., pers. comm.

$T = 3.5$°C

$P = 10.5$ MPa

$C_{sat} = 69.8$ mmol/L

$D = 10^{-5}$ cm^2/s

T, P, C_{sat} = ?
z = 1 mm

T = 0°C
P = 12 MPa
$C_{sat} = 53.7$ mmol/L
z = 2.3 mm

z = 0.179 mm

z = 2.08 mm

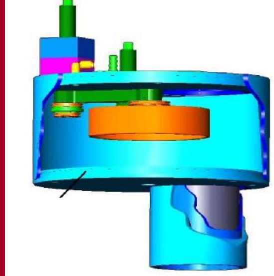
Egorov et al. (1999)

this study

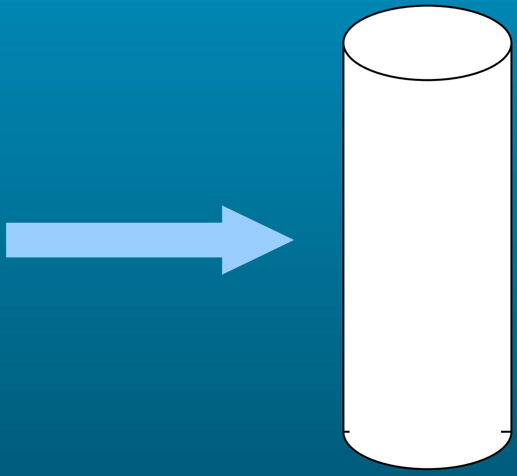
Rehder et al. (2004)

this study

Comparison with earlier data

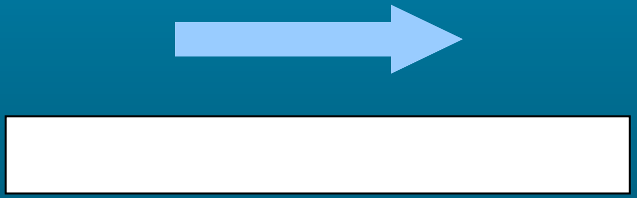


Ocean experiment:



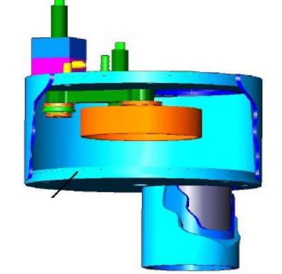
cylindrical hydrate specimens in cross flow

Lab:



plain surfaces in parallel flow

Conclusion/outlook



- Dissolution experiments demonstrate that hydrate dissolution in undersaturated seawater at P-/T-conditions within the HSF is diffusion and not reaction controlled.

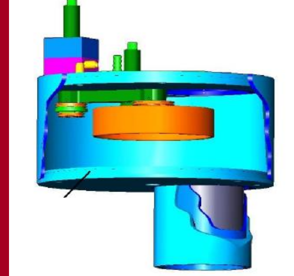
- Based on the experimental data, a k_d/u^* correlation was obtained, which excellently agrees with and is thus validated by an earlier correlation obtained from dissolution experiments with alabaster plates.

- The validated correlation permits an accurate prediction of the dissolution rates of smooth and clean methane hydrates exposed to a flow of undersaturated seawater for a broad range of oceanic conditions.

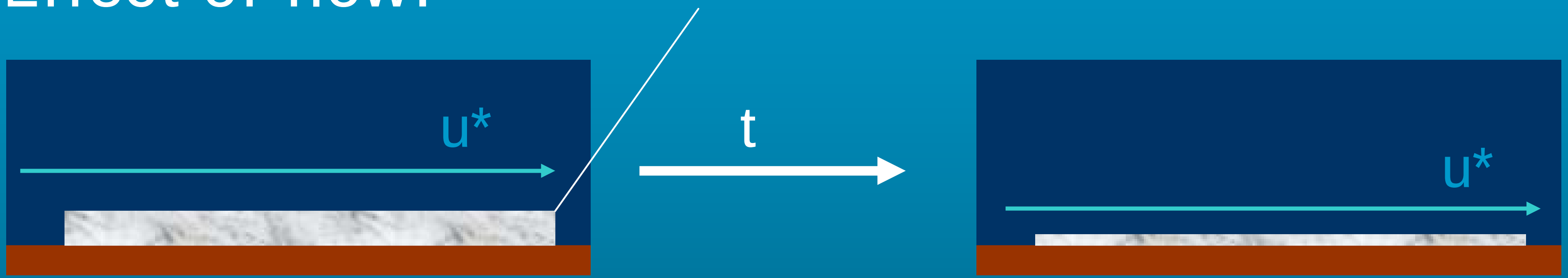
- Comparison with earlier data and postulations shows significant discrepancies. In one case this was due to a different sublayer thickness, which for lack of available data has been poorly constrained before.

- Future studies should address the role of inhibitors such as sediments or bacterial mats covering most natural gas hydrates.

Relevant Experiments I



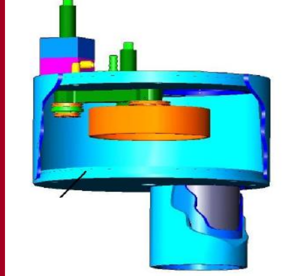
Effect of flow:

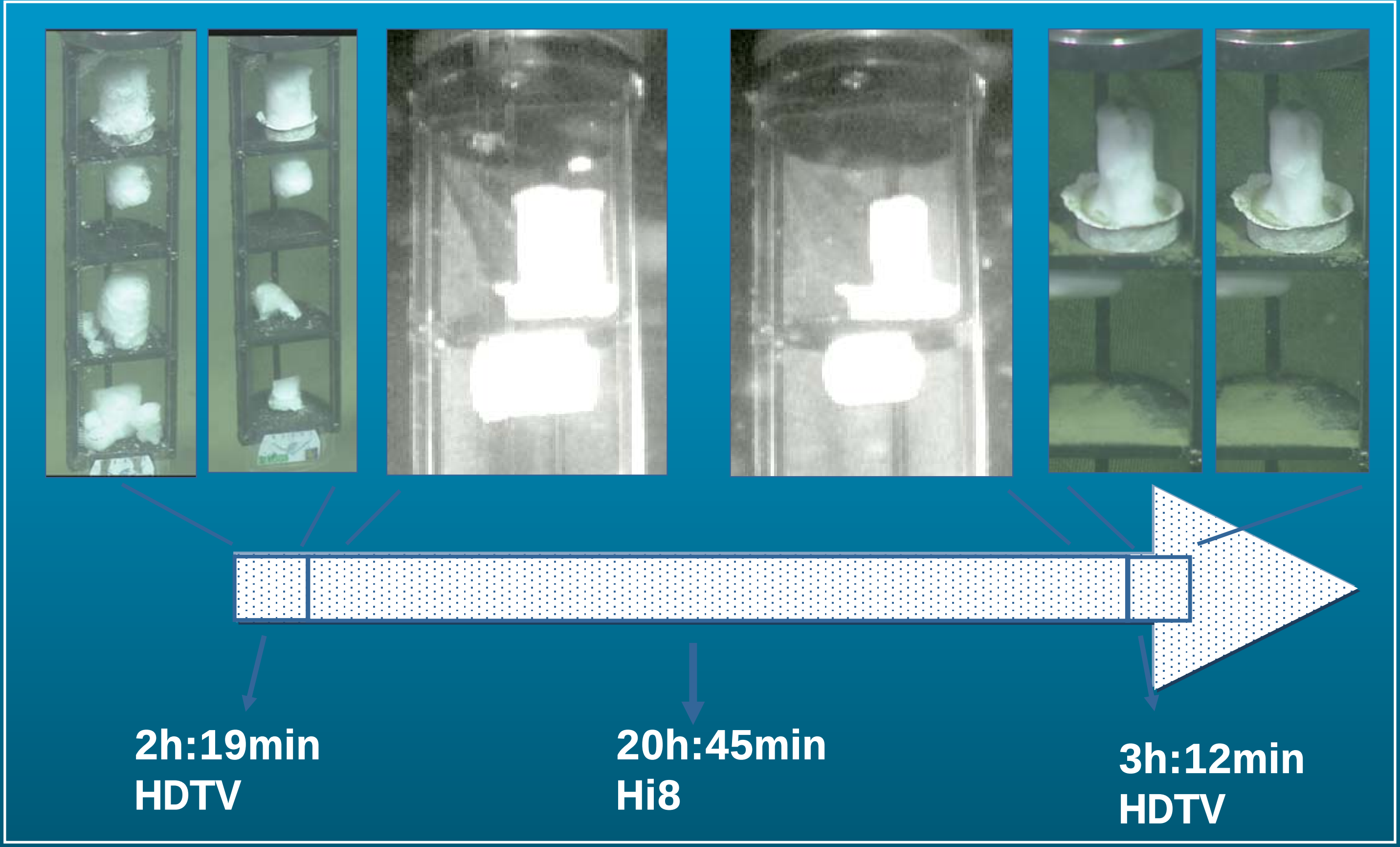


- Flux of Ca and SO_4 determined from mass loss of the alabaster
- A diffusive boundary layer model was assumed to explain mass loss.
- $k = 0.078\ Sc^{-2/3}\ u^*$

GRL 1987, 14, 1131-1134

Relevant Experiments II





$$F = D/z\,(C_{sat} - C_{t0})$$

$z(CO_2) = z(CH_4)$,

$D(CO_2) = D(CH_4)$,

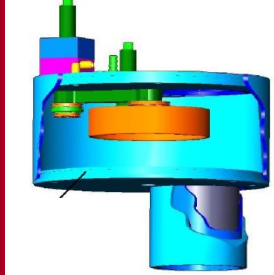
$C_{t0}=0$

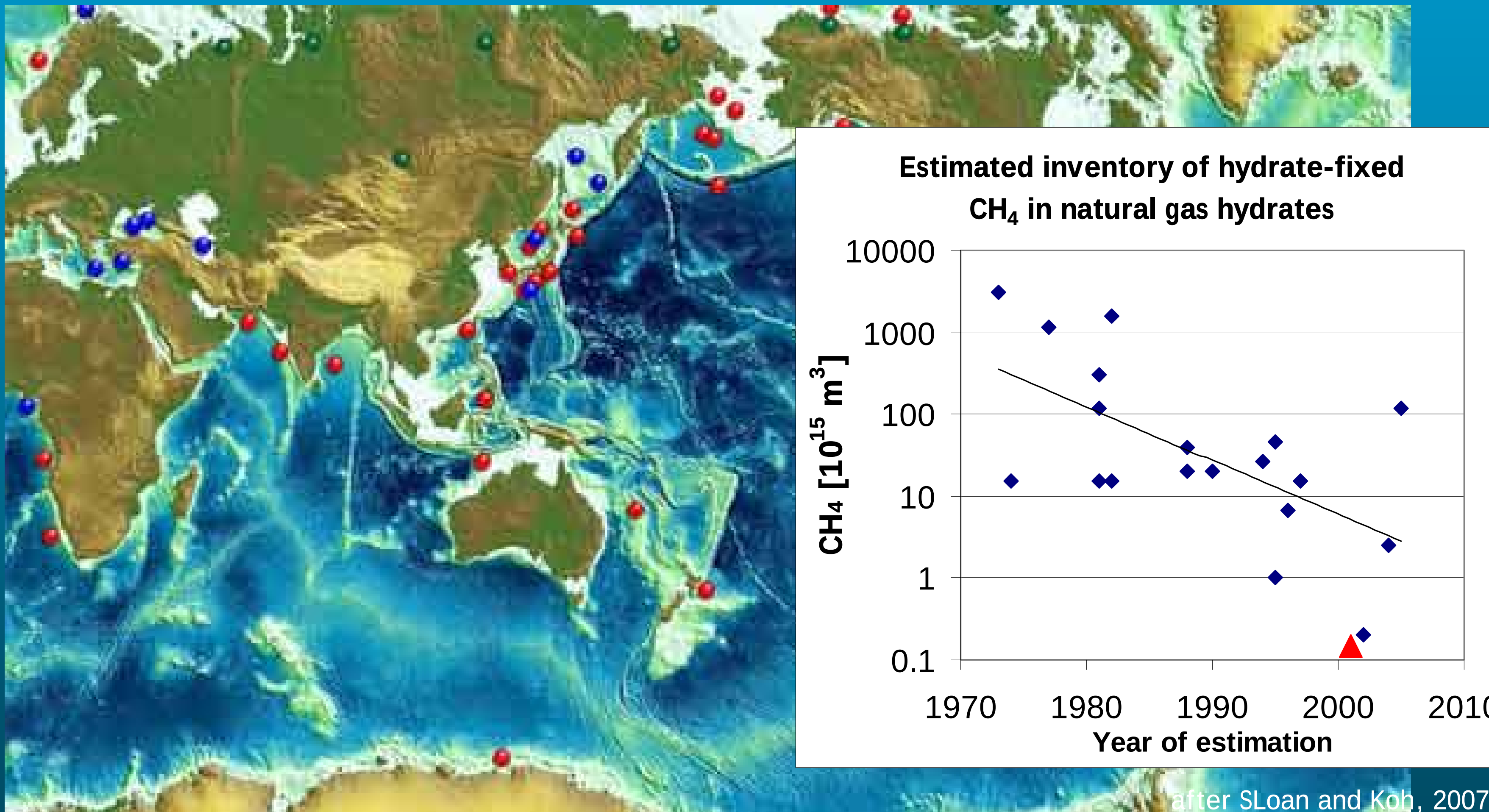
$$F(CO_2)/F(CH_4) = C_{sat}(CO_2)/C_{sat}(CH_4)$$

- Results of the field experiment fit well into a diffusive boundary layer model
- Dissolution of hydrates appears to be diffusion limited, not by kinteics of a chemical reaction

Rehder et al. (2004)

Idea/Motivation

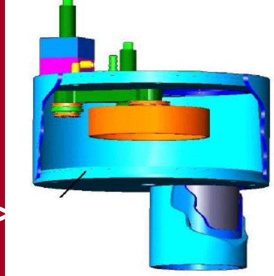




after SLoan and Koh, 2007

J. Greinert, IFM-GEOMAR

Comparison with earlier data



current speed: 1.6 cm/s ->

u* = 0.07 cm/s

D = 10^{-5} cm^2/s

T, P, C_{sat} = ?
z = 2.3 mm

21.7 m^3

Egorov et al. (1999)

T = 2.0°C
P = 30 MPa
C_{sat} = 57.6 mmol/L
z = 2.3 mm

17.4 m^3

this study

current speed: 1.75 cm/s ->

u* = 0.08 cm/s

T = 3.5°C

P = 10.5 MPa

C_{sat} = 69.8 mmol/L

D = 10^{-5} cm^2/s

z = 0.179 mm / z = 2.08 mm

370 µmol / 30.6 µmol

Rehder et al. (2004)

z_{ocean}/z_{lab}

$\stackrel{!}{=}$

$Flux_{lab}/Flux_{ocean}$

z_{ocean}/z_{lab} = 11.6

$Flux_{lab}/Flux_{ocean}$ = 11.1

z = 2.08 mm

33.4 µmol

this study